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Rational interjecting of Na and S co-catalyzed TiO_2 based nanofibers: Presence of surface layered TiS_3 shell grains and sulphur induced defects for efficient visible-light driven photocatalytic properties.

Kugalur Shanmugam Ranjith*, Tamer Uyar*

Institute of Materials Science & Nanotechnology and UNAM–National Nanotechnology Research Center, Bilkent University, Ankara, 06800,

Supportive information

Analysis of super oxides and hydroxyl radical's quantification:

The method was similar to the former PC activity test. NBT (100 mM, exhibiting an absorption maximum at 259 nm) was used as the indicator to determine the amount of $O_2^{\cdot-}$ generated by the co-catalysed nanocatalyst [25]. The NBT was stored for no longer than one day at 4 ˚C. After respective illumination for different periods of time, 1 mL of the suspension was sampled and injected into a quartz vial. The concentration of the NBT (the product resulting from the reduction of NBT by $O_2^{\cdot-}$) was measured using a UV-Vis spectrophotometer at 257 nm. Exposure tests were run for different time periods, for up to 150 min as the PC degradation test was carried out with NBT replacing the dye.

The formation of hydroxyl radicals (.OH) on the surface of Na and S co catalysed TiO_2 NF was detected by PL using terephthalic acid as the probe molecule. 75 W Xe lamp was used as the light source. Terephthalic acid readily reacts with .OH to produce a highly fluorescent product, 2-hydroxyterephthalic acid. This technique has been used in radiation chemistry, sonochemistry, and biochemistry for the detection of .OH generated in water. The method relies on the PL signal at 425 nm arising from the hydroxylation of terephthalic acid with .OH generated at the water/catalyst interface. The PL intensity of 2-hydroxyterephthalic acid is proportional to the amount of .OH radicals produced in water. The method is rapid, sensitive, and specific, and needs only a simple standard PL instrument. The experimental procedures were similar to those used in the measurement of photocatalytic activity except that the aqueous solution of RhB was replaced by an aqueous solution of 5×10^{-4} M terephthalic acid and 2×10^{-3} M NaOH. The UV irradiation or visible light irradiation was continuous and sampling was performed at given time intervals for analysis. The solution was analysed after filtration on a Perkin Elmer LS55 fluorescence spectrophotometer. The product of the terephthalic acid hydroxylation, 2-hydroxyterephthalic acid, gave a peak at a wavelength of about 425 nm by excitation with a wavelength of 315 nm. The intensity of the 425 nm PL peak increased with increasing irradiation [25].

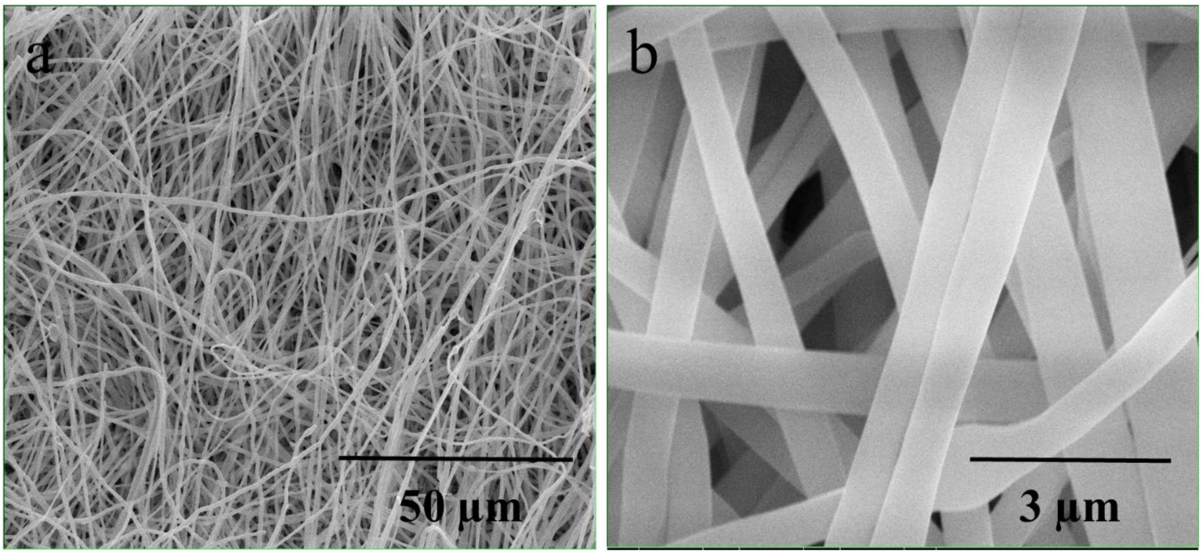

Fig. S1 Representative SEM images of as-electrospun Ti(OBu)$_4$/PVP composites nanofibers.

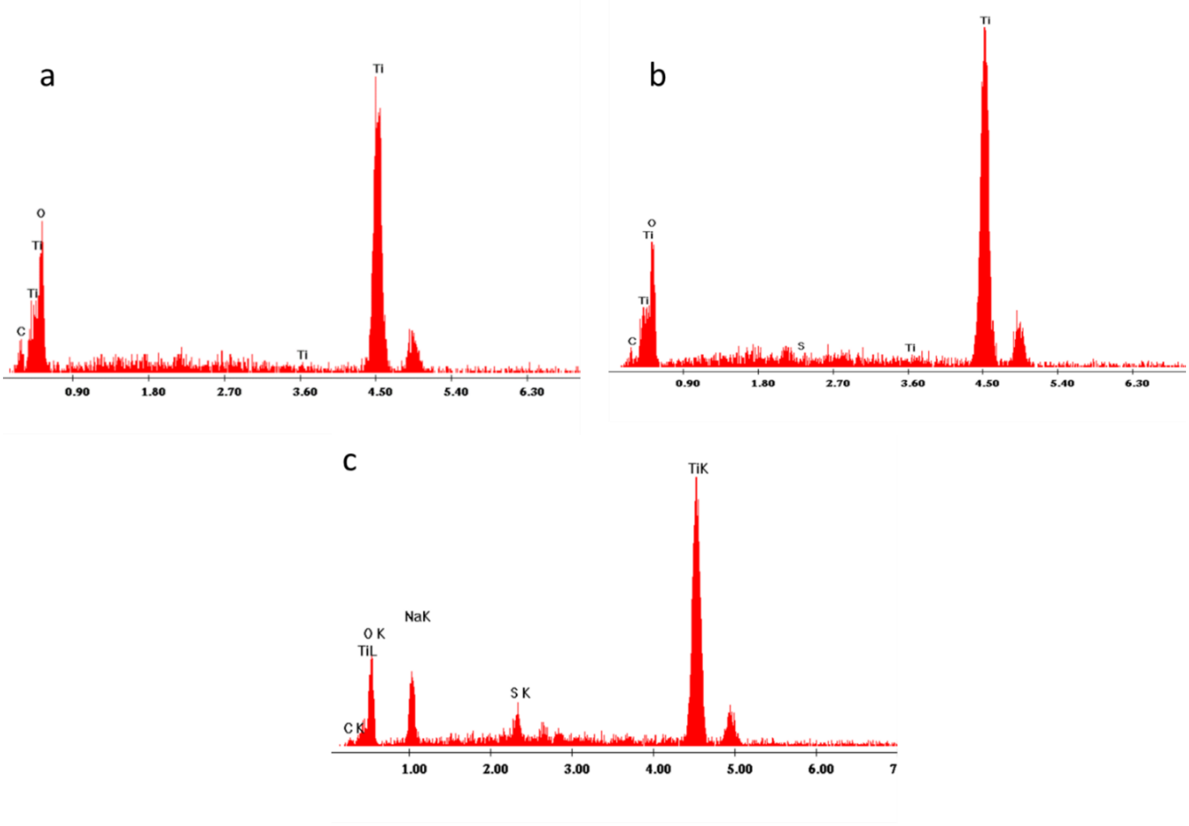

Fig. S2. EDAX spectra of (a) TiO_2 NF, (b) TiO_2 NF sulfidated with TAA and (c) TiO_2 NF sulfidated with Na_2S.

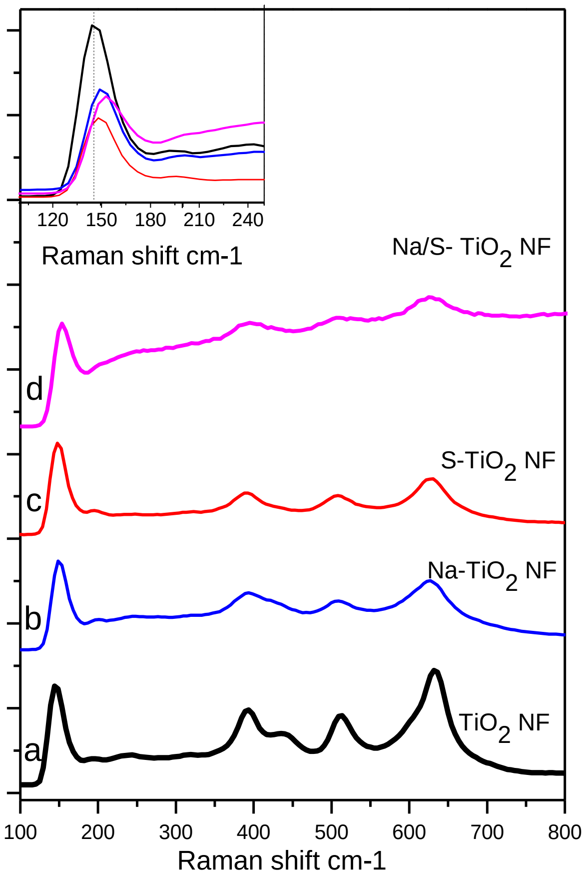

Fig. S3 Raman spectra of (a) unmodified TiO_2 NF, (b) Na-TiO_2 NF, (c) S-TiO_2 NF and (d) Na/S-TiO_2 NF.

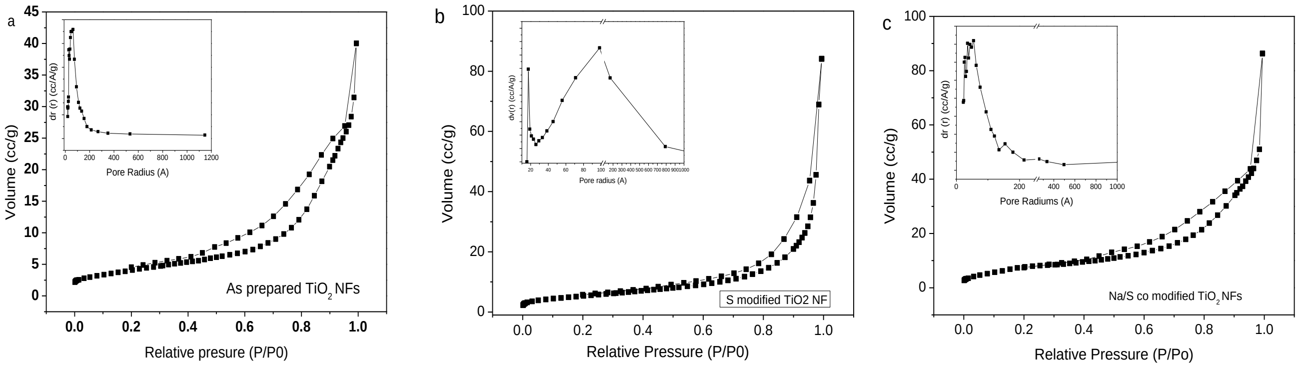

Fig. S4 BET adsorption–desorption curve for the (a) TiO_2 NF, (b) S-TiO_2 NF and (b) Na/S-TiO_2 NF. The inset shows the distribution of pore volume vs pore radius.

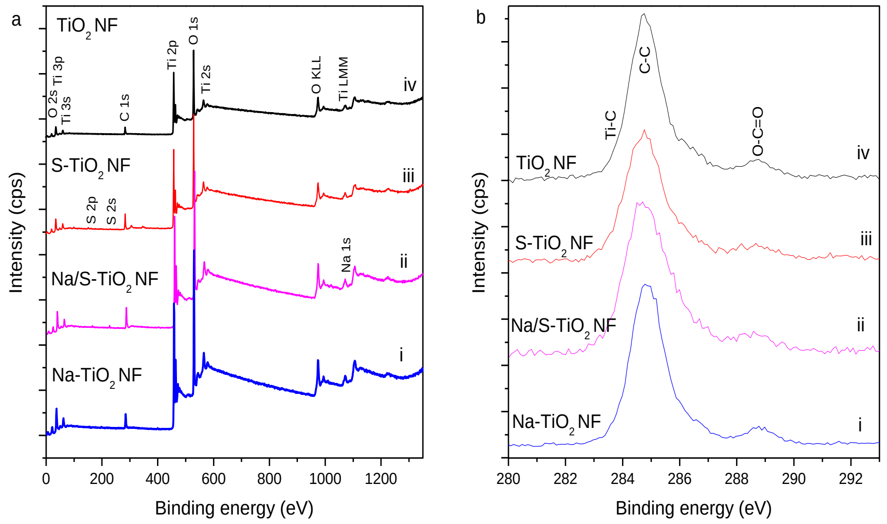

Fig. S5 XPS spectra of the pristine TiO_2 NF and surface modified TiO_2 NF samples. (a) Survey; (b) C 1s.

Table S1. XPS results presenting the position and the relative contribution of the Ti, O and S bonding for the pristine TiO_2 NF and surface modified TiO_2 NF samples.

S. No	Samples	Band gap eV	O1s nm	Atomic %	Ti 2p nm	S 2p /SO_4 ratio
1	TiO_2 NF	3.14	O_L - 530.01 Ov - 531.62 Ocl- 532.71	93 07 -	2p $^{3/2}$– 458.48 2p ½ -464.30	---
2	Na-TiO_2 NF	3.12	O_L - 530.01 Ov - 531.62 Ocl- 532.71	89 11 -	2p $^{3/2}$– 458.49 2p ½ -463.33	---
3	S-TiO_2 NF	2.58	O_L - 530.01 Ov - 531.62 Ocl- 532.71	64 32 04	2p $^{3/2}$– 458.39 2p ½ -464.19	49.43
4	Na/S-TiO_2 NF	2.28	O_L - 530.01 Ov - 531.62 Ocl- 532.71	62 30 08	2p $^{3/2}$– 458.78 2p ½ -464.58	5.67

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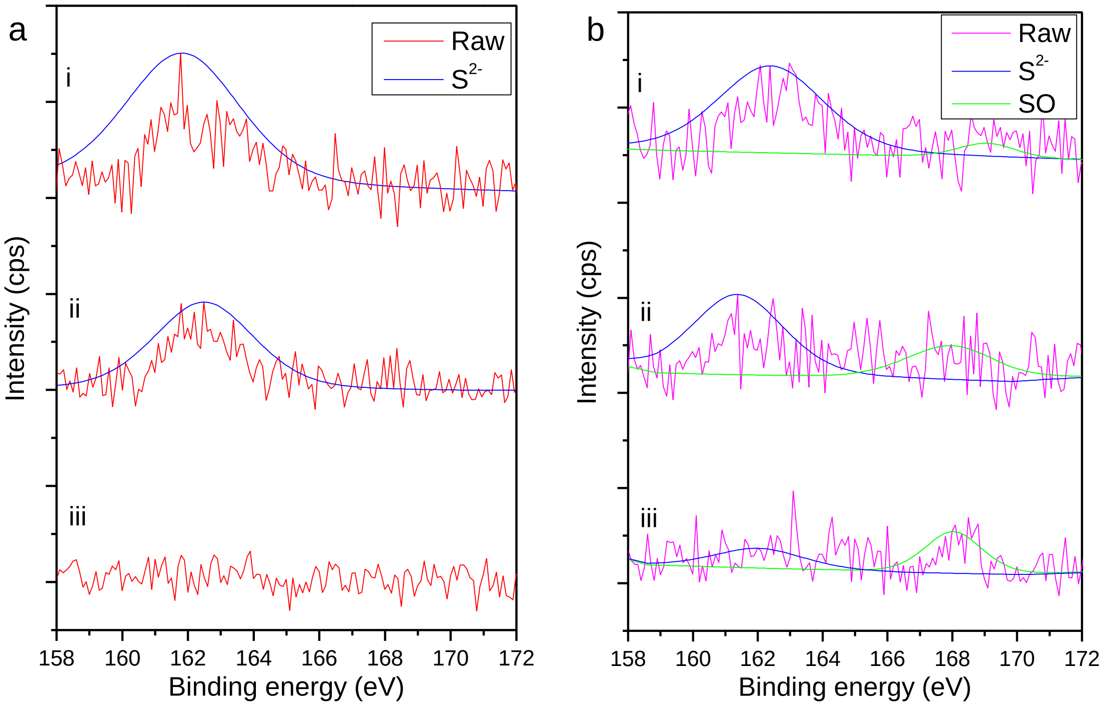

Fig. S6 XPS spectra of the S 2p spectra of the sulfur modified (a) TiO_2 NF with TAA and (b) TiO_2 NF with TAA under different ion etching process. (i) 0 sec etching (ii) 30 sec etching and (iii) 60 sec etching.

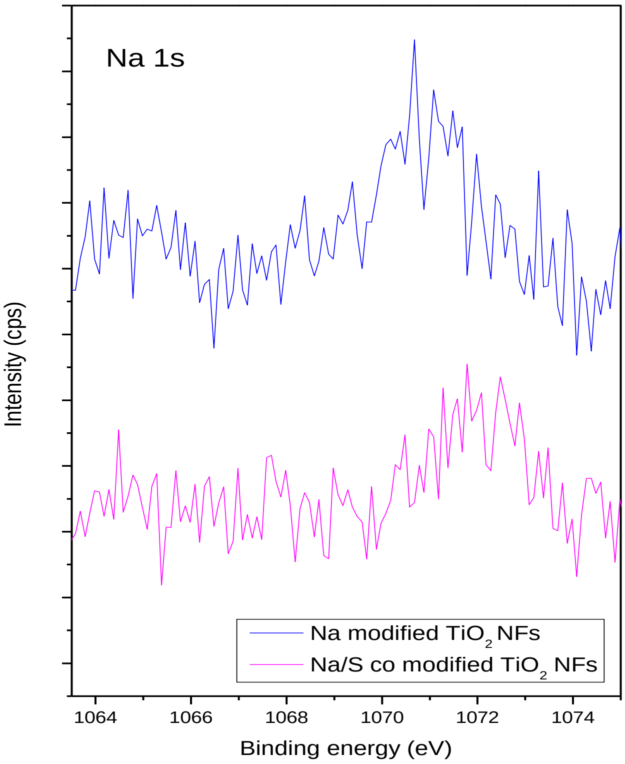

Fig. S7 XPS spectra of the Na 1S spectra of the surface modified TiO_2 NF.

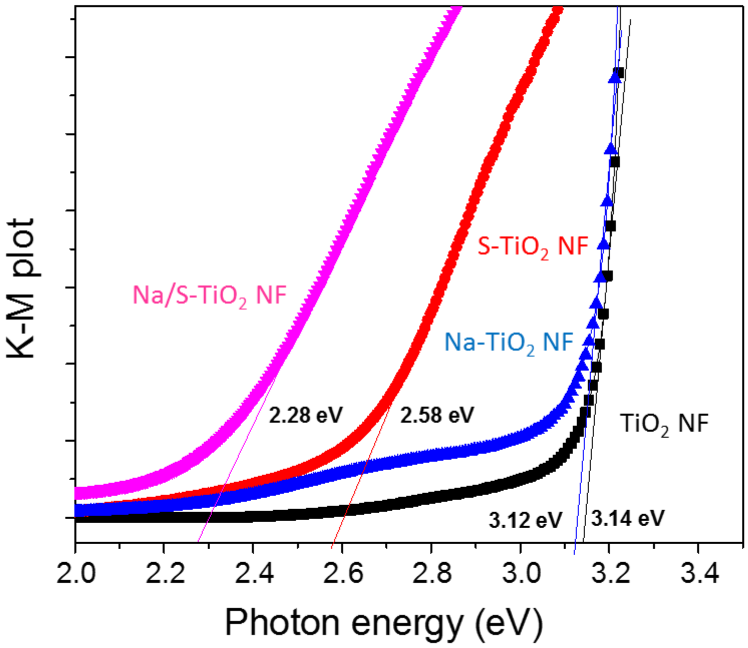

Fig. S8 K-M plot function of sulfidated TiO_2 NF to calculated the band gap.

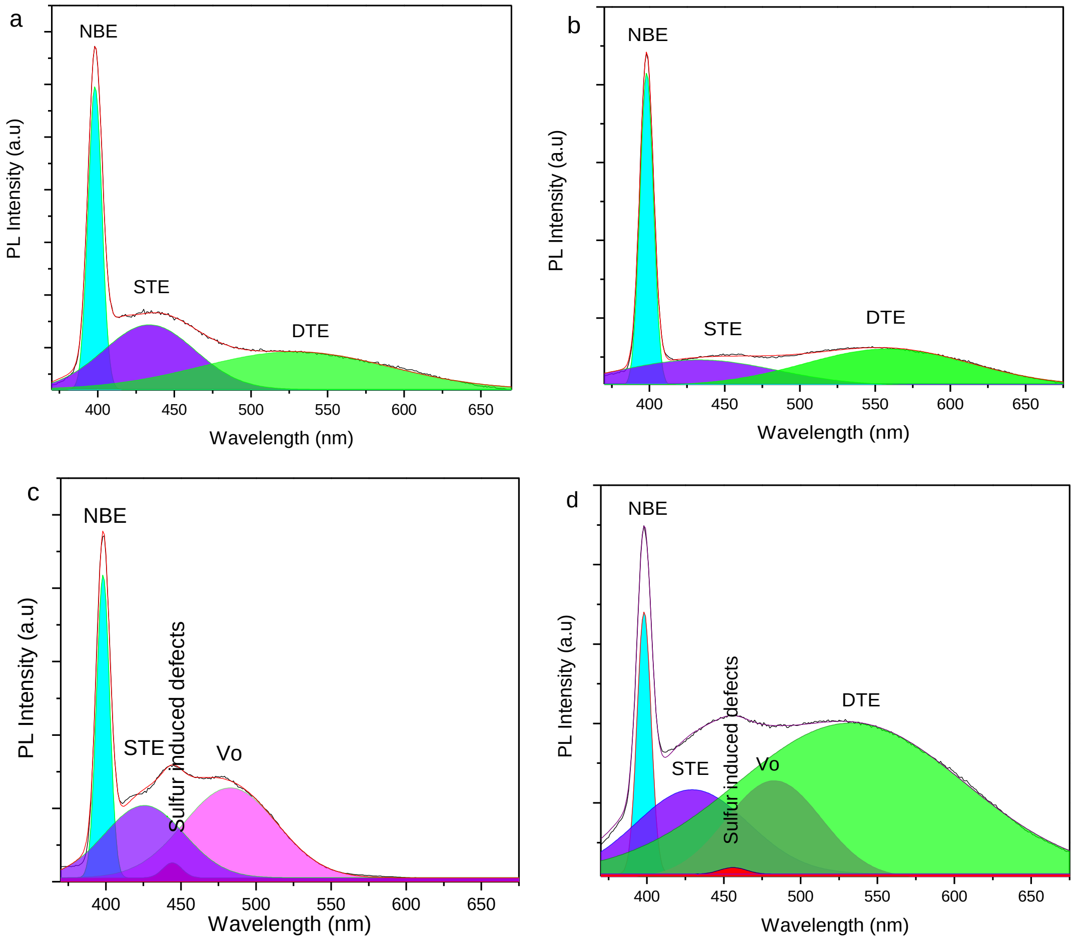

Fig. S9 Deconvoluted PL spectra of the sulfidated TiO_2 NFs (a) Pristine TiO_2 NF, (b) Na-modified TiO_2 NF, (c) S modified TiO_2 NF and (d) Na/S modified TiO_2 NF.

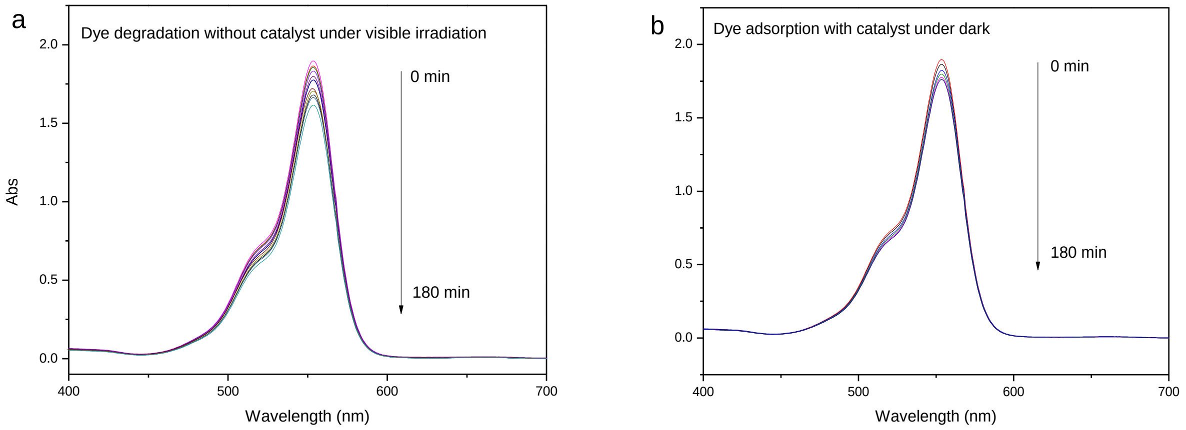

Fig. S10 Catalytic degradation of RhB (a) under visible irradiation without catalyst dark and (b) the degradation under dark with the Na/S-TiO$_2$ NF catalyst.

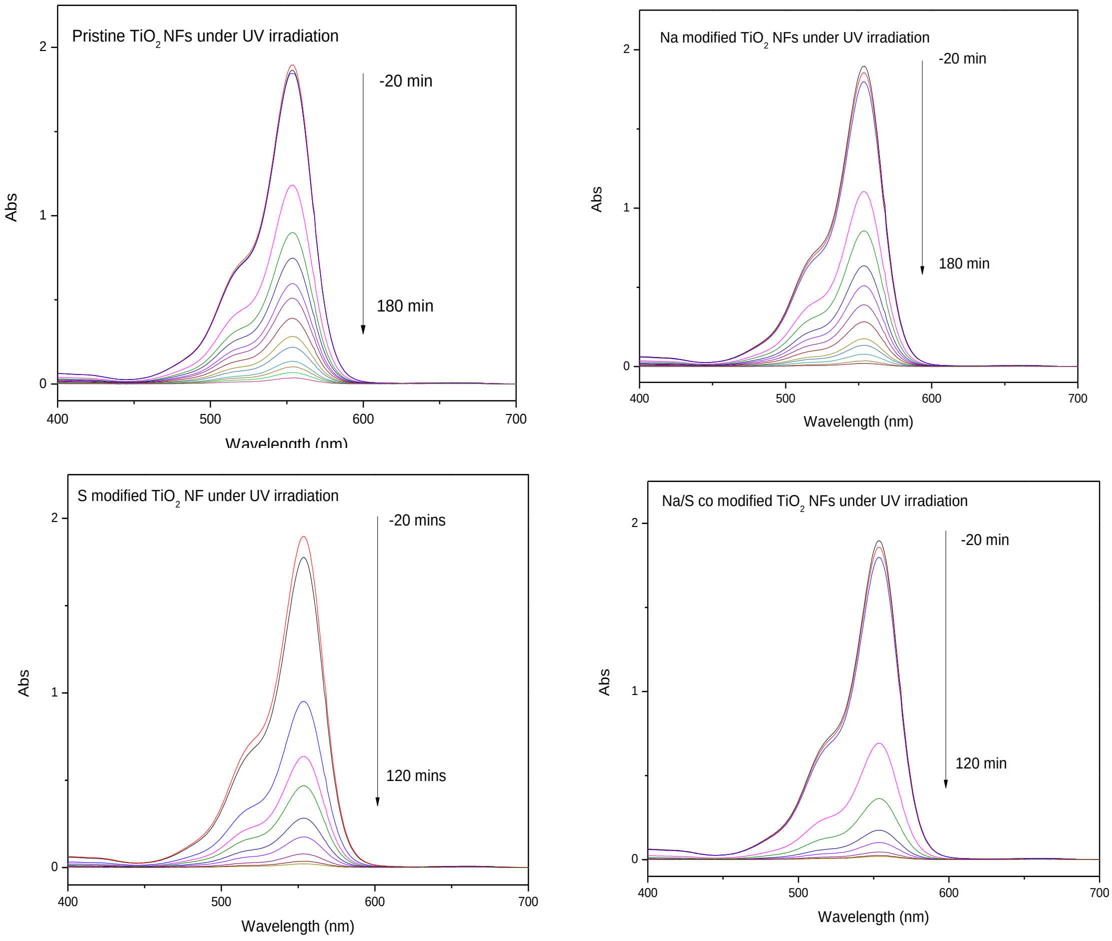

Fig S11 Representative degradation spectrum of Rhodamine B in the presence of surface modified TiO$_2$ NF during the photocatalytic measurements under UV irradiation at different time intervals.

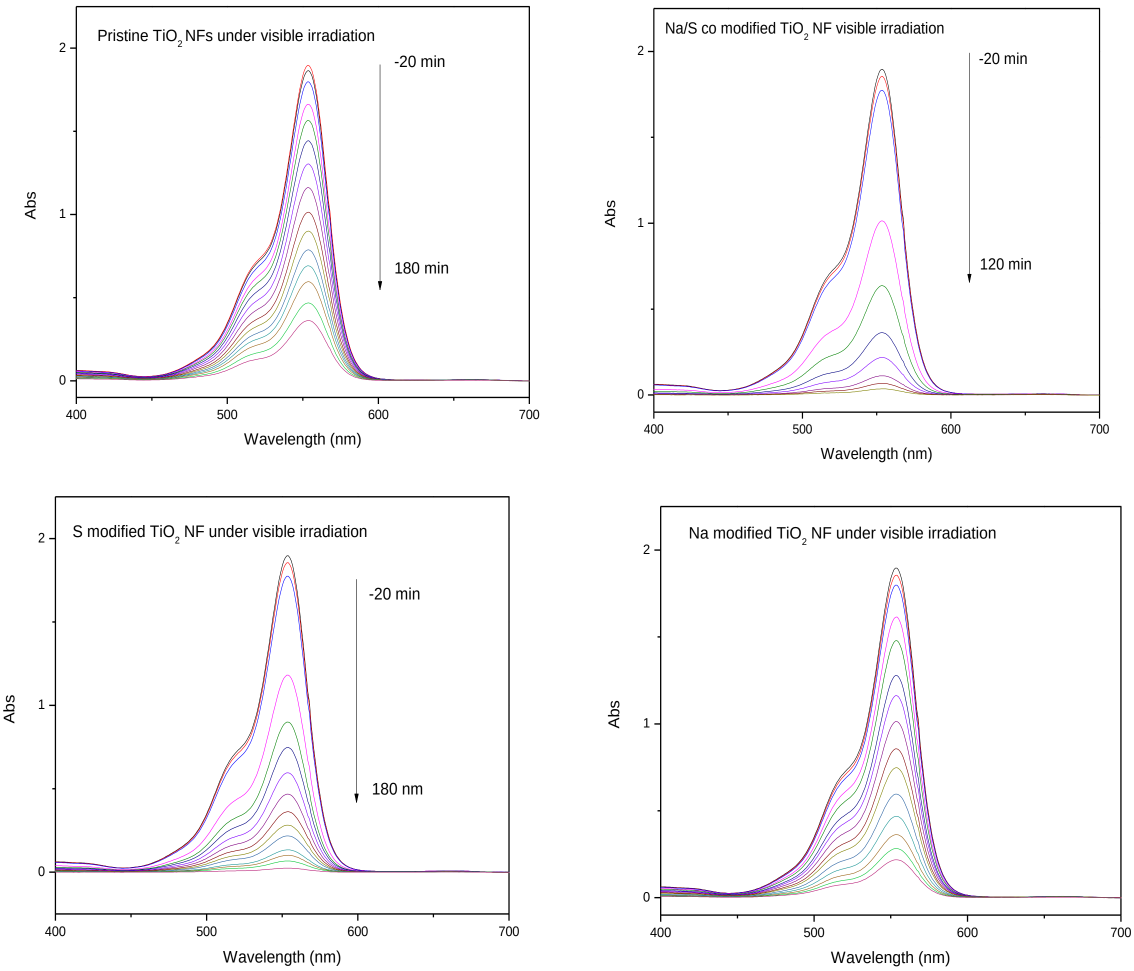

Fig. S12 Representative degradation spectrum of Rhodamine B in the presence of surface modified TiO_2 NF during the photocatalytic measurements under visible irradiation at different time intervals.

Table S2. Photo responsive properties of S functionalised TiO_2 NF

S. No	Hybrid Nano fibers	Band edge absorbance	Degradation efficiency under UV in 90 min ($\lambda = 365$ nm)	Degradation efficiency under Visible in 90 min ($\lambda > 400$ nm)	Degradation Rate (min^{-1}) ($\lambda = 365$ nm)	Degradation Rate ($\lambda > 400$ nm)
1	TiO_2	400.3 nm	79.89 %	45.12 %	0.0174	0.0076
2	Na-TiO_2	409.4 nm	85.76 %	54.83 %	0.0218	0.0088
3	S-TiO_2	513.6 nm	95.30 %	79.59 %	0.0313	0.0185
4	Na/S-TiO_2	598.7 nm	98.40 %	97.09 %	0.0472	0.0365
5	P25		57.82 %	19.17 %	0.0093	0.0024

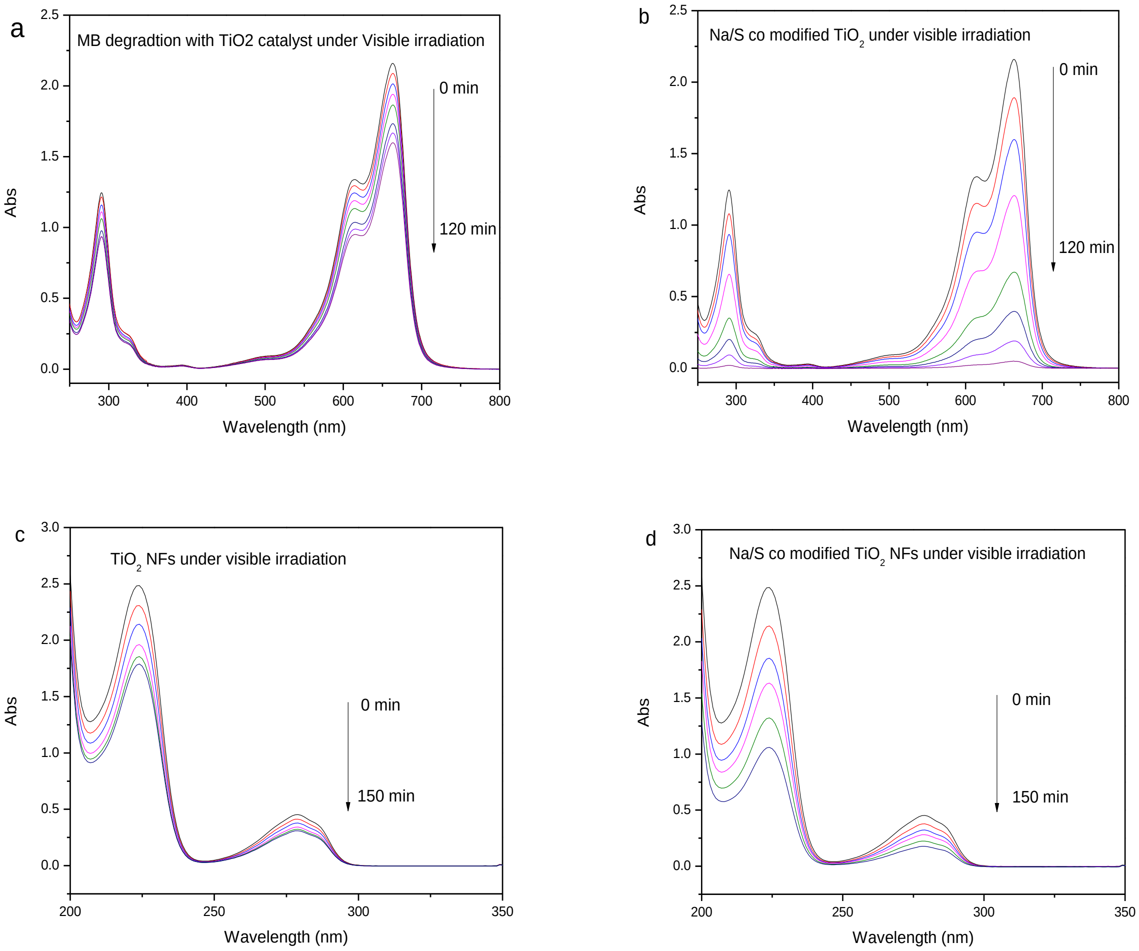

Fig. S13 (a, b) Methylene blue (MB) and (c, d) 4-chlorophenol (CP) for the TiO_2 and Na/S modified TiO_2 NF under visible irradiation.

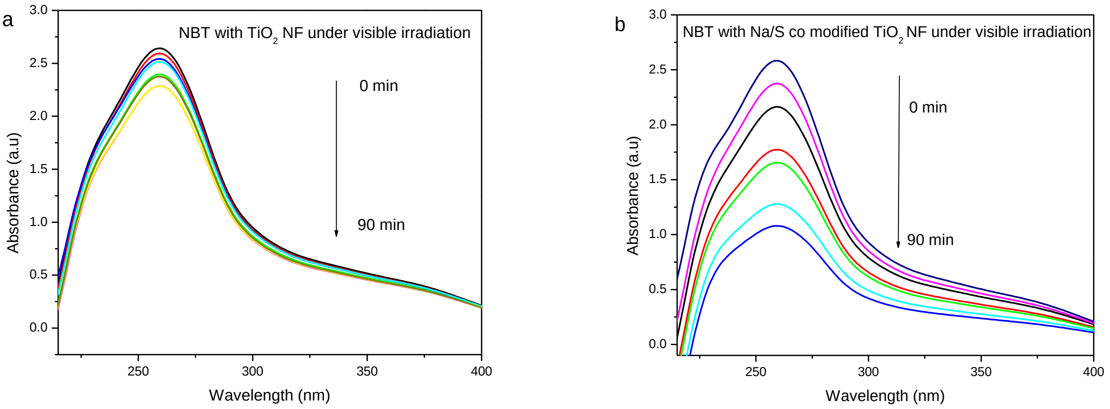

Fig. S14 UV-Vis absorption spectra of NBT in (a) TiO_2 NF and (b) Na/S modified TiO_2 NF in 90 mins of visible irradiation.

Table S3. Calculated CB and VB Positions of TiO_2 and surface modified TiO_2 NF

Sample	Band gap	CB (eV)	VB (eV)	CB off set (eV)
TiO_2 NF	3.14	-0.63	2.54	---
Na-TiO_2 NF	3.12	-0.61	2.54	---
S-TiO_2 NF	2.58	-0.18/-0.63	2.46	0.45
Na/S-TiO_2 NF	2.28	-0.08/-0.63	2.20	0.55

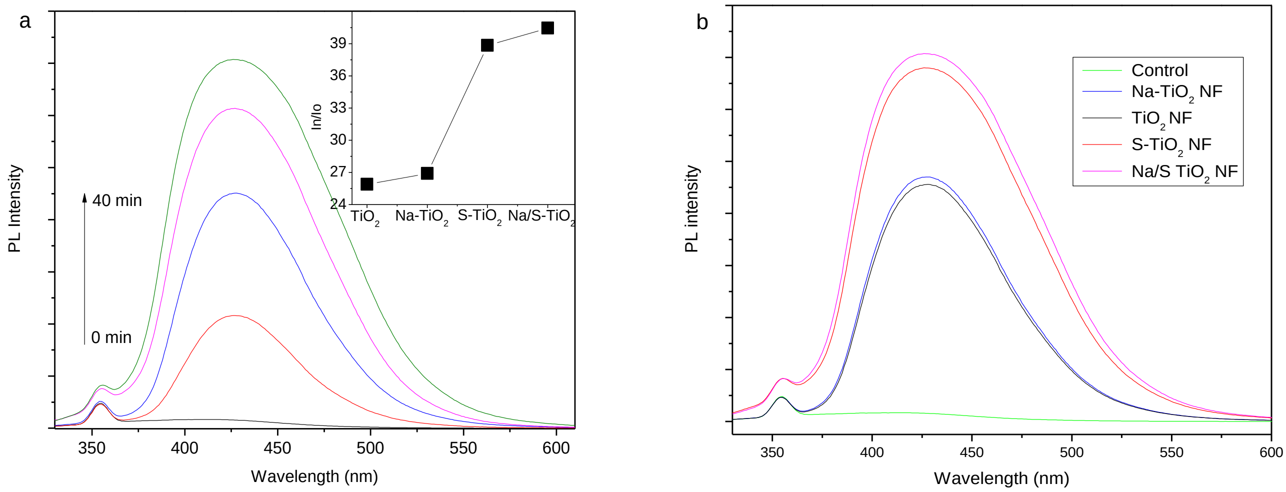

Fig. S15 PL spectra of the teraphthalic acid -OH product over the (a) Na/S co modified TiO_2 NF under visible irradiation and (b) on different surface modified TiO_2 NF under visible irradiation for 40 mins. Inset show the Id/Io ratio of the different surface modified TiO_2 NF under 40 mins of visible irradiation.

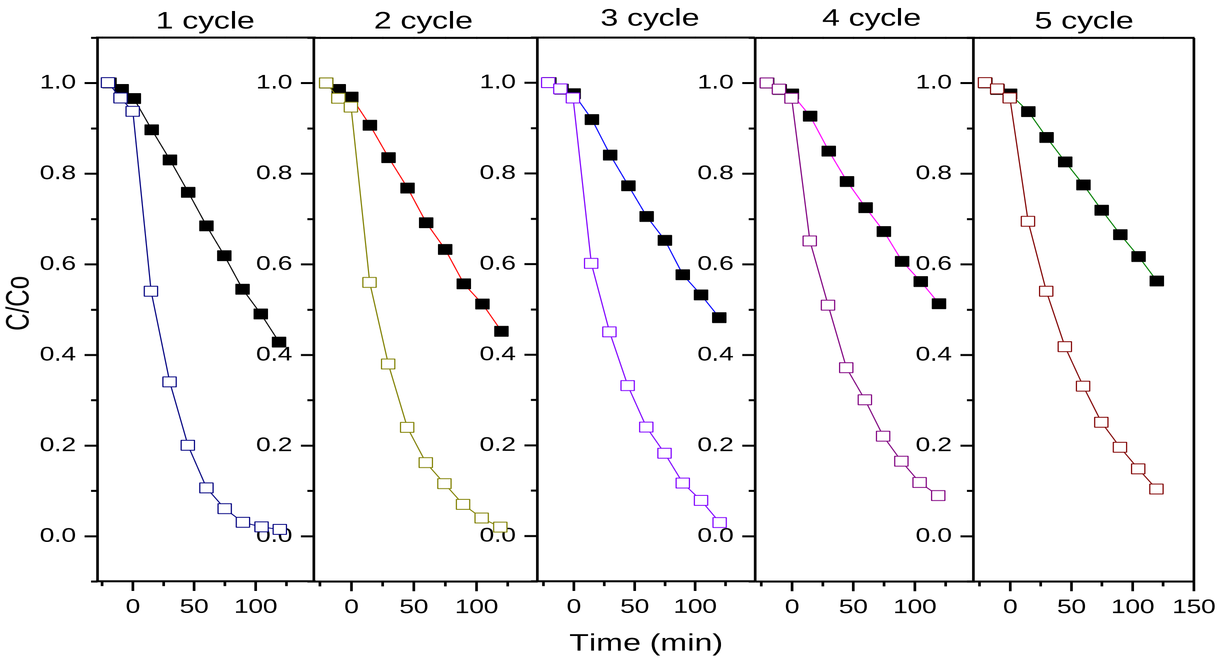

Fig. S16 Recyclic catalytic properties of TiO_2 and Na/S modified TiO_2 NF upto 5 cycles reusable PC activity

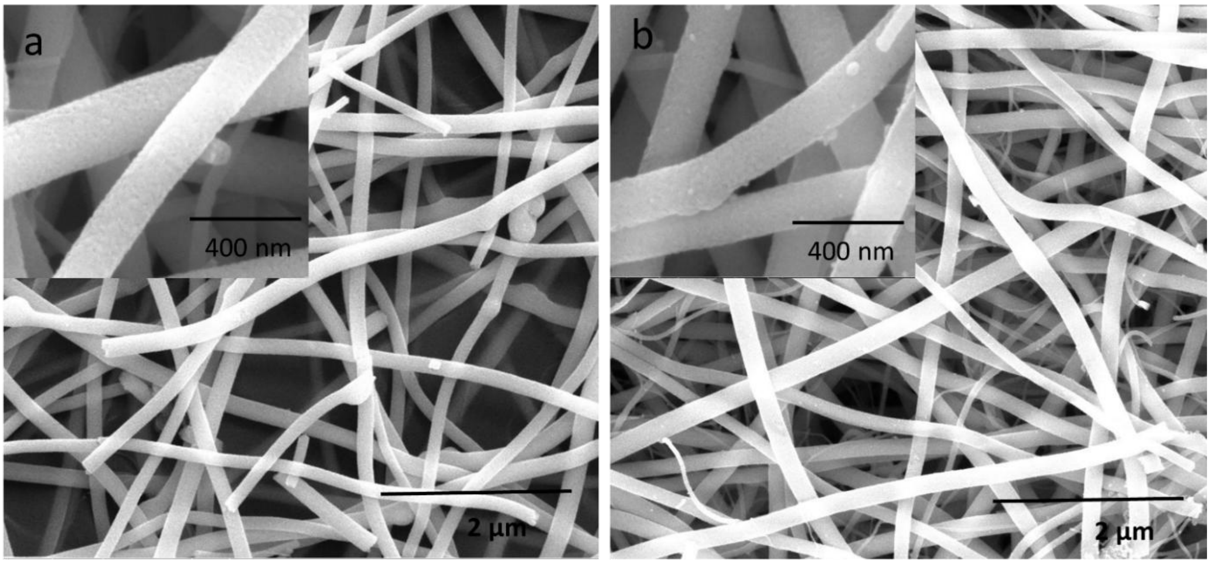

Fig. S17 Representative SEM images of electrospun derived (a) TiO_2 and (b) Na/S modified NF after photocatalytic measurements.

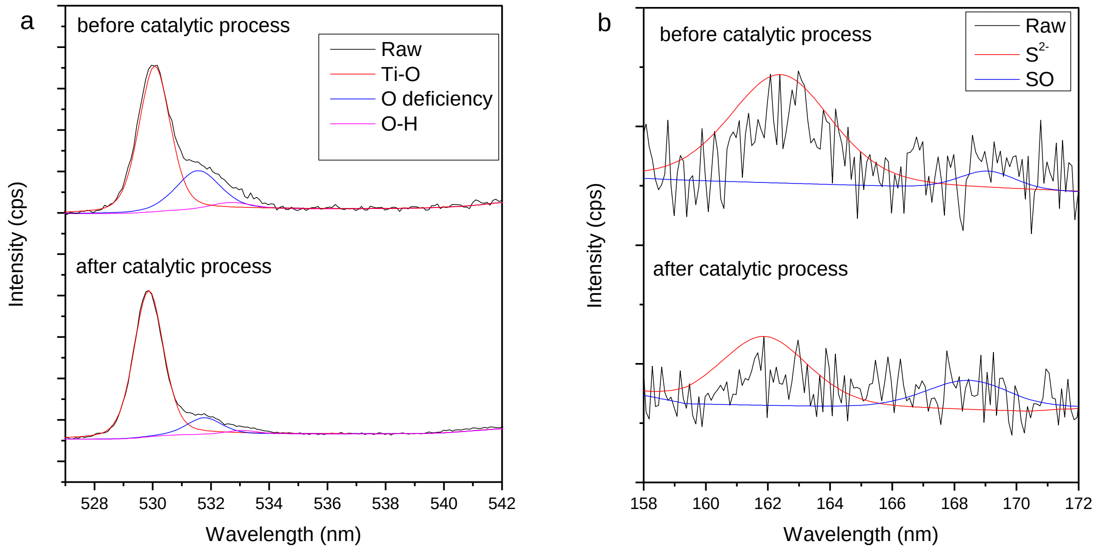

Fig. S18 XPS spectra of O 1s (a) and S2p (b) in Na/S modified TiO_2 NF before and after photocatalytic activity.